# SYNTHESIS AND PHYSICAL CHARACTERIZATION OF SIMPLE AND HIGHER ORDERED PEROVSKITES

Transition metal oxides (TMOs) belong to one of the most important classes of condensed matter systems and have been investigated for over half a century. TMOs continuously provide a remarkable playground for investigation for new physical and chemical properties[1-3]. The novel properties with potential technological applications exhibited by TMOs are namely, superconductivity, colossal magnetoresistance, giant dielectric constant, ferroelectricity, ferroelasticity, ferromagnetism, multiferroicity, optical, catalytic etc. Such properties originate from the strong electron-electron interactions and correlations in these so called strongly correlated electron oxides which also includes the interaction between lattice, charge, spin and orbital degrees of freedom. For such electronic correlations, the physical properties of these oxides cannot be captured within the framework of one-electron band theory. Among the TMOs, the perovskites based TMOs with general formula $ABO_3$ are of special type of complex oxides, where B-site cation is surrounded by six oxygen anions forming $BO_6$ octahedron. In simple perovskites the octahedral framework extended in three dimensions through vertex sharing, where the interstitial positions of these octahedral are occupied by A-site cation with dodecahedral coordination (see Fig. 1).

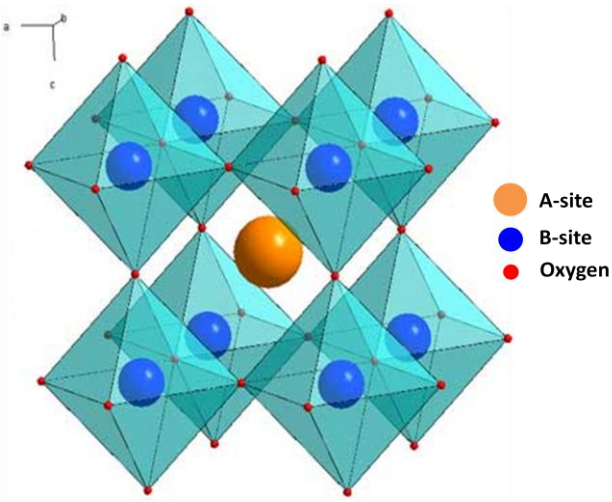


Fig. 1: Schematic view of the simple perovskite structure.

The high flexibility of the perovskite structure provides a huge scope to substitute both the A-site and B-site cations of variable size and valencies. In case of trivalent cation in A-site, the valence of B-site is fixed to three valency. Hence, accommodation of heterovalent cations in A-site results mixed valency in B-site. The prevalence of mixed valency in B-site is of prime importance, from the view point of electronic structure of the system and its manipulation. In addition of such mixed valency another important feature is the size of the A-site cations, which also plays primordial role on structure-property relationship in perovskite family of compounds. Most importantly, depending on the charge and size of cations in both the A- and B-sites different kinds of ordering phenomena may takes place in the perovskite structure leading to the modulation of crystal structure. By judicial manipulation of the A-site cationic ratio and B-site cations, it is possible to achieve several structural modifications like layered perovskite structure, double perovskite structure ($AA'B_2O_6$) and triple perovskite ($AA'B_3O_9$) and quadruple perovskite ($A'A_3B_4O_{12}$). However, achievement of structures is always a challenging issue. The major

emphasis in this thesis will be given to synthesis and characterization of double and quadrupole perovskites in addition of the simple one.

The higher ordered perovskites, namely quadrupole perovskite with the general formula $A'A_3B_4O_{12}$ became the topic of intense research in recently years due to their unusual electrical and magnetic properties as well as the inter-coupling between these two parameters popularly known as magnetoelectric coupling. Materials with such properties with inter-coupling between different parameters are known as multiferroics, which are able to perform multiple tasks at a time. However, the design of such materials is not a trivial job. A member of the quadrupole perovskite family, $CaMn_3Mn_4O_{12}$ has recently been reported to exhibit highest magnetodielectric coupling, which attracts interest of the researchers.[4]

The quadrupole perovskites, $A'A_3B_4O_{12}$ have a very special type of structure (Fig. 2); where the A'-site has dodecahedral coordination (typical for simple perovskite structure), while the A-site shows a peculiar square planar 4-fold) coordination housing a Jahn-Teller active ion, such as $Cu^{2+}$ or $Mn^{3+}$ and B is in octahedral coordination. B-site can house a large variety of transition metal or main group elements. The 4-fold coordination of A is attained by the large distortion of the dodecahedral cage produced by the large buckling of the $BO_6$ octahedra, with the consequent doubling of the three crystallographic axes, resulting pseudo cubic network. Basically fixing of A-site cation in square planar coordination in the structure is the most crucial task and generally it requires high pressure and high temperature synthesis condition. These are the major obstacles to carry out extensive investigation on this family of high order perovskites. However, a few members of the family can be synthesized at ambient pressure like $CaMn_3Mn_4O_{12}$ and $CaCu_3Ti_4O_{12}$[5,6]. The latter one exhibit giant dielectric constant but it is not a multiferroic, whereas the former one exhibit multiferroism at much lower temperature (~90 K). There are

several compounds of this family have been reported to exhibit ordering at higher temperatures [7-11]]. . The oxides $CaCu_{3-x}Mn_{4+x}O_{12}$ [7,8] and $LnCu_3Mn_4O_{12}$, with Ln = La or Ce [9,10] are of high interest for their remarkable ferrimagnetic properties with high $T_C$ values ranging from ~355 K for $CaCu_3Mn_4O_{12}$ [7] to 430 K for $ThCu_3Mn_4O_{12}$ [11]. Unfortunately all these phases require very high pressure to synthesize them. However, for the applicative point of view the achievement of magnetoelectric coupling at room temperature is always desirable.

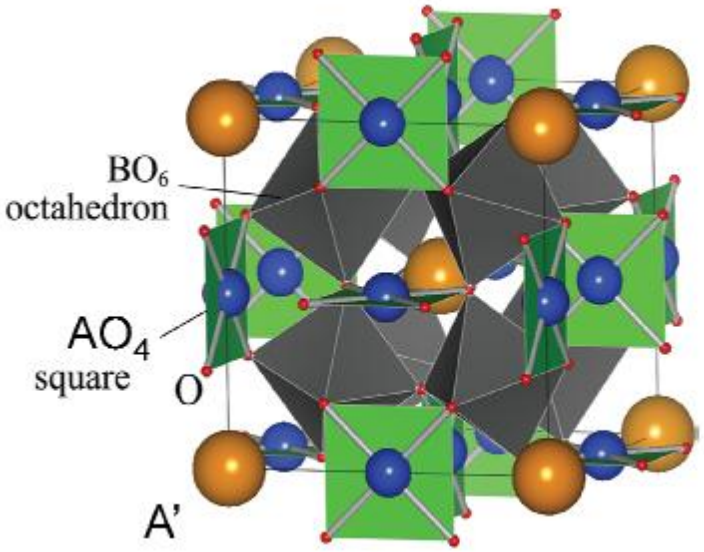


Fig. 2: Schematic view of the quadrupole perovskite structure

Our main objects of the thesis are two folds. First is to synthesis the quadrupole perovskites at ambient pressure and secondly to achieve the ordering temperature in the neighborhood of room temperature. To achieve the goal we have started the chemical substitution on $CaCu_3Ti_4O_{12}$ which can be synthesized at ambient pressure. We have been successful to obtained several single phase polycrystalline samples and rest of the work regarding its electric and magnetic study have to be done .Further research is going on so that we can successfully reach our goal.

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